Synthesis and photovoltaic performances in solution-processed BHJs of oligothiophene-substituted organocobalt complexes [([small eta]4-C4(nT)4)Co([small eta]5-C5H5)]

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Synthesis and photovoltaic performances in solution-processed BHJs of oligothiophene-substituted organocobalt complexes $[(\eta^4\text{-}C_4(n\text{T})_4)Co(\eta^5\text{-}C_5H_5)]$†

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We describe an efficient synthetic route toward novel organocobalt complexes $[(\eta^4\text{-}C_4(n\text{T})_4)Co(\eta^5\text{-}C_5H_5)]$ with n = 1, 2, 3 thiophene rings. Solution-processed bulk heterojunctions solar cells based on CpCoCb(3T)$_4$:PCBM blends achieve power conversion efficiencies of up to 2.1%.

Organic solar cells (OSC) based on polymer bulk heterojunctions (BHJ) proved to be a versatile strategy to engineer efficient and low-cost photovoltaic devices.[1] Power conversion efficiencies (PCEs) in the range 6–8% have been attained using single BHJ devices using solution-processed polymer/fullerene blends. A tandem cell based on a low band gap polymer has been recently reported to exhibit a certified PCE as high as 10.6%.[1g]

Meanwhile, BHJs made of small organic molecules emerged as a new approach with the advantages over polymers of a better control of the molecular design, a higher purity, an improved structural organization and an absence of batch-to-batch variations.[2] A wealth of small organic dyes such as squaraines,[3] porphyrins,[4] diketopyrrolopyrroles,[5] or oligothiophenes,[6,7] to name a few, have been experimented in solution-processed BHJs. Note that these small organic molecules are acting as donor (p-type) constituents of the BHJ, often in combination with a fullerene derivative as the acceptor (n-type) although non-fullerene acceptors such as perylenes were also thoroughly investigated.[8] A PCE of 6.7% has been recorded under AM 1.5 global irradiation (100 mW cm^{-2}) with a BHJ device made from DTS(PTTh$_2$)$_2$, a thiadiazole derivative, blended with PC$_{70}$BM.[2b] This high efficiency originates essentially from an intense optical absorption over the entire visible spectrum and an appropriate morphology leading to a high hole mobility (0.12 cm^2 V^{-1} s^{-1}). Very recently, by using the same thiadiazole dye, the PCE of a BHJ solar cell in an inverted structure reached values as high as 7.88%,[9] while record PCEs of over 8.0% were attained using a benzodithiophene derivative.[6] These encouraging results pave the way towards small molecule-based OSCs with PCEs exceeding 10%.

Among the plethora of small organic molecules currently investigated as active materials for OSCs, organometallic complexes represent an attractive class of materials. In particular organometallic dyes based on noble metals (such as Ru, Rh or Ir) are extensively utilized as photosensitizers solar cells of various types.[10] Besides, organometallic complexes based on 3d-transition metals (such as Co, Ni, Cu, Zn, *etc.*) are also studied for solar energy conversion, in particular the large family of metallophthalocyanines.[11] When attached to organic ligands 3d-transition metals induce metal–ligand charge transfer (MLCT) transitions spanning over the visible and near infrared spectra.[10b] Finally, note that 3d metals also possess intra-3d transitions absorbing strongly in the visible region that have been used to sensitize wide bandgap oxides such as ZnO, TiO_2 or $SrTiO_3$, in view of solar energy conversion.[12]

We present here the synthesis and photovoltaic behaviour of novel oligothiophene-substituted organocobalt complexes with general formula $[(\eta^4\text{-}C_4R_4)Co(\eta^5\text{-}C_5H_5)]$. The central Co(I) atom is linked to a cyclopentadienyl (η^5-C_5H_5, noted Cp) and a cyclobutadienyl (η^4-C_4R_4, noted Cb) ligands. Both planar Cp and Cb ligands are located at the apex of each other to form a 3D sandwich molecule. The Cb rings are substituted by four peripheral oligothiophene units nT of various lengths (n = 1, 2, 3). The introduction of π-conjugated oligothiophene substituents on the Cb ring is expected to contribute to the MLCT transitions and to improve the charge transport in the BHJ.[13] Finally, we note that CpCoCb complexes substituted by appropriate groups on both the Cp and Cb rings have been extensively reported as altitudinal molecular rotors,[14] supramolecular cages,[15] or catalysts.[16]

The organic solar cells under study here are based on BHJs prepared by mixing the CpCoCb(nT)$_4$ complexes together with

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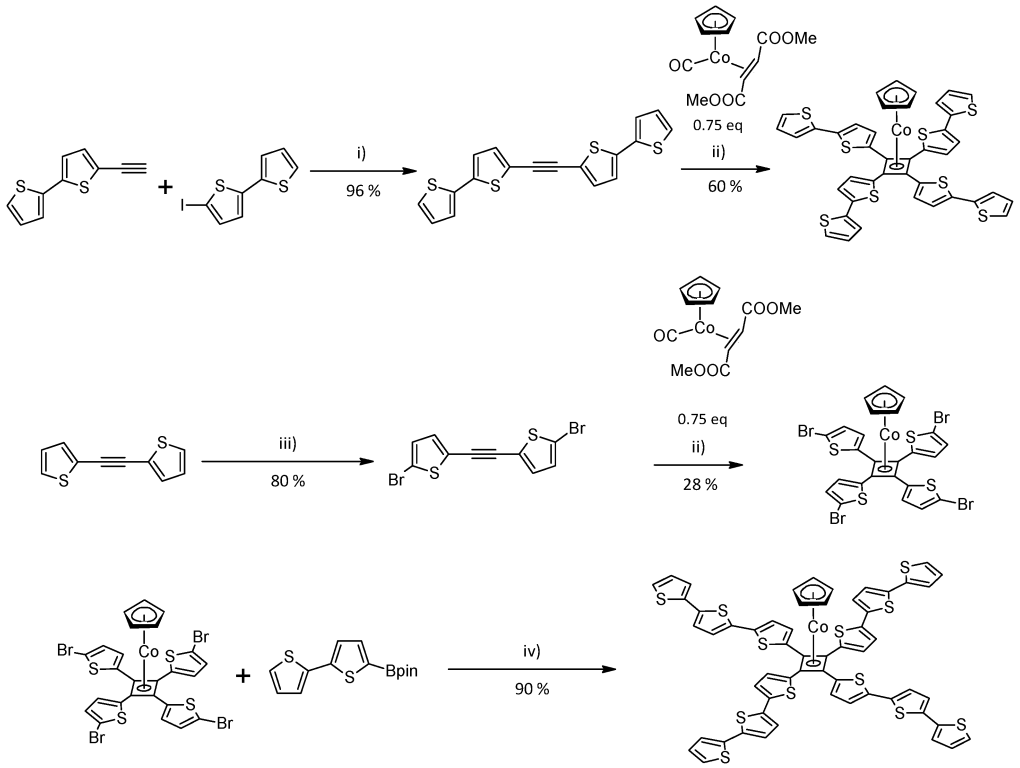
† Electronic supplementary information (ESI) available: Experimental details on the synthesis and electronic properties the of CpCoCb(nT)$_4$ complexes, fabrication and testing of the photovoltaic devices. See DOI: 10.1039/c4cc03530e



Scheme 1 Synthetic pathways to CpCoCb(nT)$_4$ with n = 2, 3. (i) 10 mol% $PdCl_2(PPh_3)_2$, 10 mol% CuI NEt_3, RT, 24 h. (ii) 14/1 THF/EtOH, microwave 150 °C, 30 min (P = 80 W). (iii) 2.2 eq. BuLi, THF, −40 °C, 30 min, Br_2, RT, 2 h. (iv) 20 mol% $PdCl_2$(dppf), 16 eq. K_2CO_3, THF/H_2O, reflux 5 days.

[6,6]-phenyl-C60-butyric acid methyl ester (PCBM) as the acceptor material. The CpCoCb(nT)$_4$ complexes are soluble in usual organic solvents and can be easily processed *via* spin-coating. The device architecture was set to be {glass/ITO/PEDOT:PSS/CpCoCb(nT)$_4$:PCBM/LiF/Al}. PCEs of up to 1.87% under 75 mW cm^{-2} and 2.12% under 22 mW cm^{-2} were recorded with CpCoCb(3T)$_4$.

The three CpCoCb(nT)$_4$ complexes are conveniently synthesized according to an original strategy (Scheme 1). The synthesis of the shorter analog CpCoCb(1T)$_4$ has already been described elsewhere,[17] while 2T and 3T are novel compounds. The key step is the use of CpCo(CO)(DMFU)[18] (with DMFU = dimethylfumarate) engaged in a [2+2] cycloaddition under microwave conditions developed in our laboratory.[19] Precursors for CpCoCb(1T)$_4$ and CpCoCb(2T)$_4$ were synthesized using a Sonogashira type coupling. A first attempt to synthesize CpCoCb(3T)$_4$ using the same approach was carried out but the bis(3T)-acetylene precursor proved to be very difficult to be isolated due to an ultra-low solubility (<5 mg L^{-1} in DCM). Therefore we investigated a second route based on a Suzuki coupling following the [2+2] cycloaddition, leading successfully to the target CpCoCb(3T)$_4$ product. Surprisingly this complex was highly soluble in organic solvents (~20 mg mL^{-1} in CH_2Cl_2 and 35 mg mL^{-1} in 1,2-dichlorobenzene) in spite of the four 3T units per molecule. The absorption spectra of the three CpCoCb(nT)$_4$ compounds (Fig. 1) exhibit a broad band with a bathochromic shift of λ_{max} from 1T (254 nm) to 2T (354 nm) and to 3T (399 nm). One can note that the molar extinction coefficient of CpCoCb(3T)$_4$ reached values as high as 10^4–10^5 L mol^{-1} cm^{-1} over the 300–600 nm range. Cyclic voltammetry experiments were performed on the three

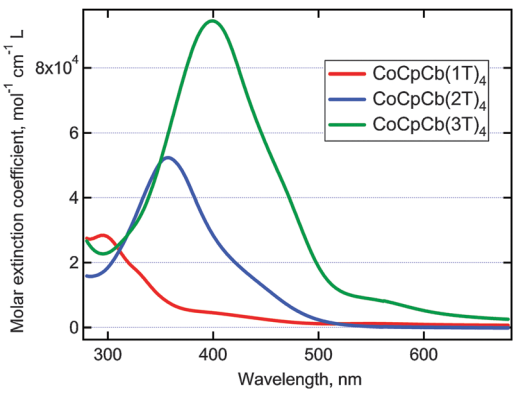


Fig. 1 Absorption spectra of the three CpCoCb(nT)$_4$ complexes (n = 1, 2, 3) in dichloromethane.

CpCoCb(nT)$_4$ derivatives in order to complete their electronic structures (Fig. S1, ESI†). As expected optical absorption (λ_{max} and ε) and the oxidation potential $E^{ox}_{1/2}$ scale the nT chain length from n = 1 to 3. The energetic parameters deduced from optical and electrochemical data allow us to determine the HOMO levels using formula (1)[20] (Table S1, ESI†):

$$E_{HOMO} = -(1.4 \pm 0.1) \times q(E_{ox} - E_{ref}) - (4.6 \pm 0.08)\ \text{eV} \quad (1)$$

The energetic data of the CpCoCb(3T)$_4$ complex are then associated with the HOMO–LUMO levels of PCBM and the

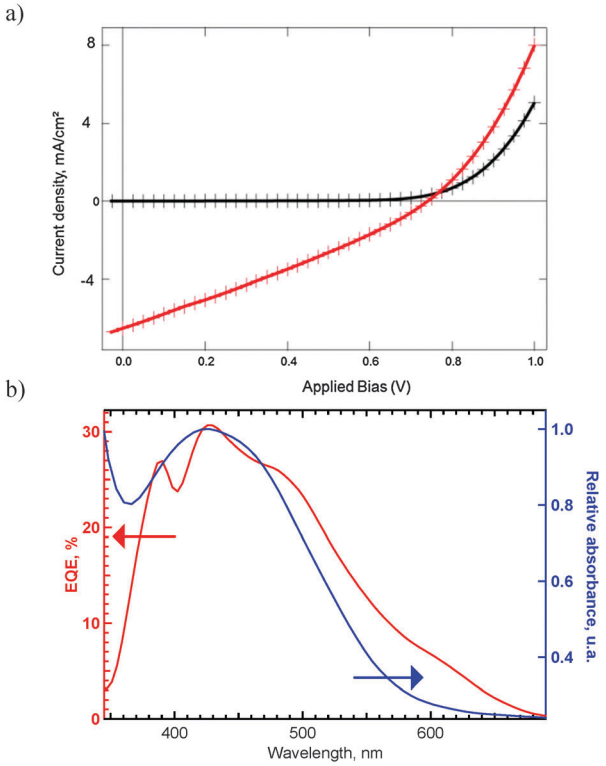


Fig. 2 (a) *I*/*V* response of an OSC based on a CpCoCb(3T)$_4$:PCBM BHJ in the dark (black) and under white light irradiation (AM 1.5G, 75 mW cm^{-2}, red). (b) EQE (red) and absorption (blue) spectra of a BHJ device based on a CpCoCb(3T)$_4$:PCBM blend.

Fermi levels of the ITO and Al electrodes used in the devices. The energetic diagram of a BHJ solar cell based on CpCoCb(3T)$_4$ as the donor or and PCBM as the acceptor (Fig. S2, ESI†) shows a typical staircase profile favourable for an efficient PV effect under visible light irradiation.

The *I*/*V* characteristics of OSCs based on CpCoCb(*n*T)$_4$ in the dark and under white light illumination (AM 1.5 G, 75 mW cm^{-2}) are presented in Fig. 2a. In the dark the *I*/*V* curve reveals excellent diode behaviour over the −2.0 V/+2.0 V range (Fig. S4, ESI†). Increasing the length of the four *n*T units (*n* = 1, 2, 3) results in a considerable increase in the PCE up to 1.9% for CpCoCb(3T)$_4$ (Table 1). When exposed to lower incident powers, the PCE increases up to 2.1% under 22 mW cm^{-2} (Fig. S5, ESI†). Similarly, in open air V_{oc} is higher for the 3T derivative (608 mV) as compared to the shorter 1T (102 mV) and 2T (331 mV) derivatives. The current density is also improved with longer *n*T units, up to J_{sc} = 6.2 mA cm^{-2} for CpCoCb(3T)$_4$ under N_2. However, for the three complexes the fill factor (FF) remains low with average values in the range 27–32%. Surprisingly, thermal annealing of the CpCoCb(3T)$_4$ devices (see experimental details in the ESI†) leads to a reduced J_{sc} = 2.2 mA cm^{-2}. The low PCEs measured in open air indicate that the complexes photooxidize as previously reported for some thiophene derivatives.[21]

Table 1 PV characteristics under AM 1.5 G (75 mW cm^{-2}) of the CpCoCb(*n*T)$_4$ complexes

CpCoCb(*n*T)$_4$ complex	J_{SC} (mA cm^{-2})	V_{OC} (mV)	FF (%)	PCE (%)
n = 1	0.015[a]	102[a]	27[a]	0.001[a]
n = 2	3.15[a]	331[a]	28[a]	0.05[a]
n = 3	1.4[a]	608[a]	30[a]	0.35[a]
	6.4[b]	732[b]	30[b]	1.87[b]
	2.2[c]	664[c]	32[c]	2.12[c]

[a] In open air. [b] Under N_2. [c] Under N_2 after annealing, under 22 mW cm^{-2}.

The EQE spectrum of OSCs based on CpCoCb(3T)$_4$ (Fig. 2b) spans all over the visible range with two maxima at 390 nm and 430 nm, as well as two shoulders at 490 nm and 600 nm. The peaks at 390 nm and 430 nm probably arise from the absorption of the four conjugated 3T arms. On the other hand the weak intensity shoulder at 600 nm is consistent with a metal–ligand charge transfer (MLCT) transition between the Co atom and the azimuthal organic ligands. Fig. 2b reveals that optical absorption in the 480–700 nm range contributes more efficiently to PV conversion as compared to the 350–480 nm range. This could arise from a longer lifetime of excitons generated by an MLCT transition due to the strong spin–orbit coupling of the Co atom that stabilizes triplet states.

In summary, three CpCoCb(*n*T)$_4$ complexes bearing four oligothiophene arms of different lengths have been synthetized and investigated as donor materials in solution-processed BHJ solar cells. In particular, devices elaborated with CpCoCb(3T)$_4$ show V_{oc} values beyond 0.7 V and reach PCEs of 1.9% and 2.1% under an incident power of 75 and 22 mW cm^{-2} respectively. Tailoring the four oligothiophene arms (length, substituents, *etc.*) of the CpCoCb(*n*T)$_4$ building block should allow us to considerably improve these promising PV performances.

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